Organometallics **2003,** *22,* 3348−3350

Synthesis, Structure, and Cyclic Voltammetric Studies of $[CpFeC_5H_4C\equiv CAlNCH_2(C_4H_3S)]_6$: The First Model Compound for the Fixation of Metal-Containing Ligands on an Aluminum Nitride Cluster[†]

S. Shravan Kumar,[‡] N. Dastagiri Reddy,[‡] Herbert W. Roesky,*[,‡] Denis Vidovic,[‡]
Jörg Magull,[‡] and Rainer F. Winter[§]

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany, and Institut für Anorganische Chemie der Universität Stuttgart,
Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received May 9, 2003

Summary: An Al−N cluster containing an assembly of six ferrocenylacetylene moieties has been synthesized and structurally characterized. The electrochemical behavior of this compound shows a single reversible oxidation wave, which suggests the electrochemical equivalence of the ferrocenylacetylene moieties.

Recently, heteronuclear mixed-valence organometallic complexes containing combinations of main-group elements and transition metals in the same molecular unit have generated great interest. They can be viewed as precursors for high-temperature superconducting materials and new semiconducting materials. These kind of molecules reported in the literature involve either direct bonding between the metals[1] or bridging by a spacer as in M−X−M,[2,3] where X is a heteroatom such as oxygen, nitrogen, or phosphorus. The metal centers in these mixed-valence bimetallic complexes not only exhibit different reactivities but also act as model compounds in materials and catalysis.[4] Anchoring active catalysts to insoluble materials cuts the loss of catalyst, makes the workup of products easier, and has influence on the catalytic process due to the Lewis acidity of the support.[5,6] The fixation of catalysts, containing active metal centers, on supports was mainly done on silicate surfaces.[7,8] This concept can also be extended to aluminum compounds containing an Al−N skeleton framework.[9] So far, these frameworks have been used as potential precursors for a wide variety of microelectronic applications.[10] Our interest lies in synthesizing soluble cluster compounds that mimic supports on which transition metals can be anchored. A few ferrocenylacetylene cluster compounds containing transition metals have been reported in the literature[11] and have been investigated by electron spectroscopy[12a−c] and cyclic voltammetry.[12] However, there have been no reports where ferrocenylacetylene moieties are assembled on an alu-

---

* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

[†] Dedicated to Professor Heinrich Nöth on the occasion of his 75th birthday.

[‡] Universität Göttingen.

[§] Universität Stuttgart.

(1) (a) St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver J. P. *J. Organomet. Chem*. **1977**, *129*, 1. (b) Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem*. **1977**, *16*, 920. (c) Clarkson, L. M.; Norman, N. C.; Farrugia, L. J. *Organometallics* **1991**, *10*, 1286. (d) Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 2575.

(2) (a) Tessier-Youngs, C.; Bueno, C.; Beachley, O. T., Jr.; Churchill, M. R. *Inorg. Chem*. **1983**, *22*, 1054. (b) Stephan, D. W. *Coord. Chem. Rev*. **1989**, *95*, 41. (c) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res*. **1987**, *20*, 167. (d) Tessier-Youngs, C.; Youngs, W. J.; Beachley, O. T., Jr.; Churchill, M. R. *Organometallics* **1983**, *2*, 1128.

(3) (a) Zheng, T. C.; Cullen, W. R.; Rettig, S. J. *Organometallics* **1994**, *13*, 3549. (b) Wong, W. Y.; Wong, W. T. *J. Chem. Soc., Dalton Trans*. **1996**, 3209. (c) Lee, S. M.; Cheung, K. K.; Wong, W. T. *J. Organomet. Chem*. **1996**, *506*, 77. (d) Hui, J. W. S.; Wong, W. T. *J. Chem. Soc., Dalton Trans*. **1997**, 2445.

(4) Fischer, R. A.; Behm, J. *J. Organomet. Chem*. **1991**, *413*, C10 and references therein.

(5) Copéret, C.; Chabanas, M.; Saint-Arroman, R. P.; Basset, J.-M. *Angew. Chem*. **2003**, *115*, 164. *Angew. Chem., Int. Ed*. **2003**, *42*, 156−181.

(6) (a) *Metal Clusters in Catalysis*; Studies in Surface Science and Catalysis 29; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986. (b) *Catalysis by Zeolites*; Studies in Surface Science and Catalysis 5; Elsevier: Amsterdam, 1980. (c) Gates, B. C. *Angew. Chem*. **1993**, *105*, 240; *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 228. (d) Ichikawa, M.; Rao, L.; Fukuoka, A. In *Catalytic Science and Technology*; Yoshida, S., Takezawa, N., Ono, T., Eds.; VCH: Weinheim, Germany, and Kodansha: Tokyo, Japan, 1991; Vol. 1, pp 111−116. (e) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalyts with Organometallic Compounds;* VCH: Weinheim, Germany,1996.

(7) Chabanas, M.; Copéret, C.; Basset, J.-M. *Chem. Eur. J*. **2003**, *9*, 971 and references therein.

(8) Ritter, U.; Winkhofer, R.; Murugavel, R.; Voigt, A.; Stalke, D.; Roesky, H. W. *J. Am. Chem. Soc*. **1996**, *118*, 8580.

(9) (a) Reddy, N. D.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem*. **2002**, *41*, 2374. (b) Reddy, N. D.; Kumar, S. S.; Roesky, H. W.; Vidovic, D.; Magull, J.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem*. **2003**, 442. (c) Zheng, W.; Roesky, H. W. *J. Chem. Soc., Dalton Trans*. **2002**, *14*, 2787. (d) Peng, Y.; Rong, J.; Roesky, H. W.; Labahn, T.; Magull, J.; Noltemeyer, M.; Schmidt, H.-G. Submitted for publication in *J. Fluorine Chem.*.

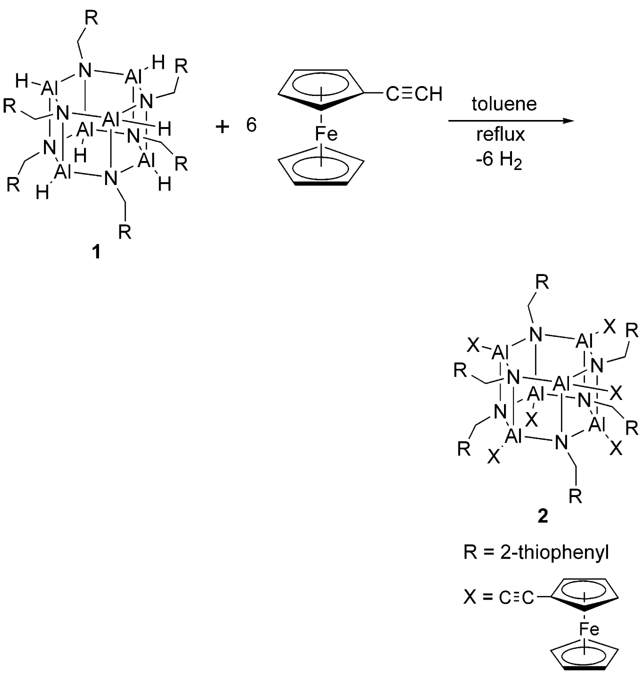
(10) (a) Boyd, D. C.; Haasch, R. T.; Mantell, P. R.; Schulze, R. K.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater*. **1989**, *1*, 119. (b) Bolt, J. D.; Tebbe, F. N. *Adv. Ceram*. **1989**, *26*, 69. (c) Bertalet, D. C.; Liu, H.; Rogers, J. W. *J. Appl. Phys*. **1994**, *75*, 5385. (d) Jones, A. C. *J. Cryst. Growth* **1993**, *129*, 728. (e) Rockensüss, W.; Roesky, H. W. *Adv. Mater*. **1993**, *5*, 443.

(11) (a) Russo, M. V.; Furlani, A.; Licoccia, S.; Paolesse, R.; Villa, A. C.; Guastini, C. *J. Organomet. Chem*. **1994**, *469*, 245. (b) Koridze, A. A.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem*. **1992**, *441*, 277. (c) Worth, G. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1992**, *11*, 501. (d) Deeming, A. J.; Felix, M. S. B.; Nuel, D.; Powell, N. I.; Tocher, D. A.; Hardcastle, K. I. *J. Organomet. Chem*. **1990**, *384*, 181.

(12) (a) Dowling, N.; Henry, P. M.; Lewis, N. A.; Taube, H. *Inorg. Chem*. **1981**, *20*, 2345. (b) Dowling, N.; Henry, P. M. *Inorg. Chem*. **1982**, *21*, 4088. (c) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 943. (d) Kotz, J. C.; Getty, E. E.; Lin, L. *Organometallics* **1985**, *4*, 610. (e) Diaz, A. F.; Mueller- Westerhoff, U. T.; Nazzal, A.; Tanner, M. *J. Organomet. Chem*. **1982**, *236*, C45. (f) Kotz, J.; Neyhart, G.; Vining, W. J.; Rausch, M. D. *Organometallics* **1983**, *2*, 79. (g) Clemente, D. A.; Pilloni, G.; Corain, B.; Longato, B.; Tiripicchio, M. C. *Inorg. Chim. Acta* **1986**, *115*, L9. (h) Schwarzhans, K. E.; Schottenberger, H. *Z. Naturforsch*. **1983**, *38B*, 1493. (i) Obendorf, D.; Schottenberger, H.; Rieker, C. *Organometallics* **1991**, *10*, 1293. (j) Kasahara, Y.; Hoshino, Y.; Kajitani, M.; Shimizu, K.; Sato, G. P. *Organometallics* **1992**, *11*, 1968.

10.1021/om030348d CCC: $25.00
Publication on Web 07/22/2003

Scheme 1



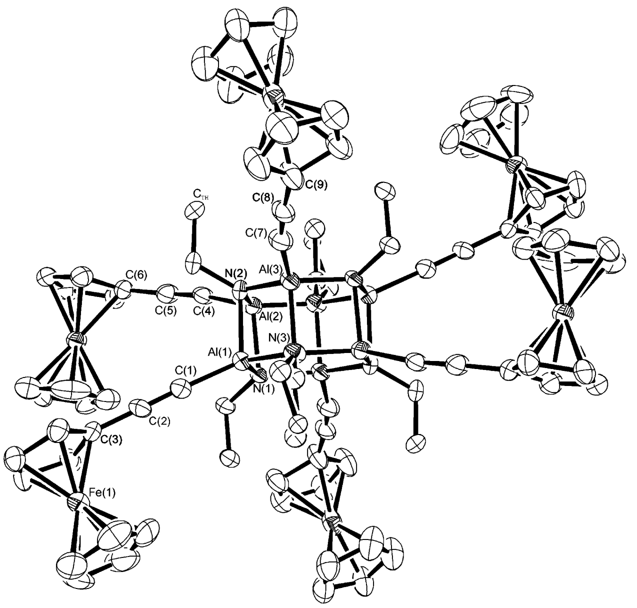


Figure 1. Molecular structure of **2** in the crystal. C_{TH} = 2-thiophenyl. Thiophenyl groups and toluene molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) = 1.887(6), Al(1)–N(2) = 1.981(5), Al(1)–N(3) = 1.882(5), Al(1)–C(1) = 1.893(6), C(1)–C(2) = 1.222(8), C(2)–C(3) = 1.444(8); C(2)–C(1)–Al(1) = 170.82(7), C(5)–C(4)–Al(2) = 166.88(6), C(8)–C(7)–Al(3) = 169.11(5), C(1)–C(2)–C(3) = 174.9(8), C(7)–C(8)–C(9) = 176.90(8), C(4)–C(5)–C(6) = 174.70(7), N(1)–Al(1)–N(2) = 92.01(2), Al(1)–N(1)–Al(2) = 87.56(2), Al(2)–N(2)–Al(3) = 123.91(2), N(3)–Al(1)–N(1) = 115.79(8), N(2)–Al(1)–C(1) = 115.00(2), N(3)–Al(1)–C(1) = 121.17(3).

minum nitride cluster. In this contribution, we report the synthesis, structure, and cyclic voltammetric studies of an Al–N cluster containing an assembly of six ferrocenylacetylene moieties.

The reaction between stoichiometric amounts of compound **1** and ferrocenylacetylene[13] under reflux conditions leads to the formation of compound **2** (Scheme 1). The reaction mixture was refluxed until the evolution of H_2 had ceased. The resulting solution was kept at 0 °C to obtain reddish brown crystals of **2**.[14] It is the only isolable compound. All six hydridic hydrogens were replaced by six ferrocenylacetylene moieties. The Al–N framework remained intact during the substitution. Compound **2** is air- and moisture-sensitive and was characterized by multinuclear NMR, mass spectrometry, IR, and elemental analysis. A strong absorption band at 2119 cm^{-1} in the IR spectrum can be attributed to the $\tilde{\nu}$(C≡C)[15] stretching frequency. The lack of absorption bands at 1860 and 3313 cm^{-1} indicates the absence of Al–H and C≡*C*–*H* bonds, respectively. No molecular ion peak is found in the EI mass spectrum.

The molecular structure of **2** in the solid state was determined by a single-crystal X-ray structural analysis.[16] **2** crystallizes in the triclinic space group $P\bar{1}$ with half of the molecule and two molecules of toluene in the asymmetric unit. An ORTEP plot of **2** is shown in Figure 1. The polyhedron contains an Al–N framework in which the aluminum and nitrogen atoms are positioned alternatively. The molecule has a center of symmetry, and two of the ferrocenyl moieties are oriented toward the central core, while the rest is projected away. The bond parameters are similar to those of the previously studied structures, and the Al–N bond lengths forming the hexagonal faces are significantly shorter than the transverse ones.[9,21,22] It is noteworthy that the C≡C–Al bond angles deviate from the expected 180° and vary significantly from each other (C(2)–C(1)–Al(1) = 170.82(7)°, C(5)–C(4)–Al(2) = 166.88(6)°, C(8)–C(7)–Al(3) = 169.11(5)°). In a similar way the C≡C–C bond angles

---

(13) (a) Rosenblum, M.; Brawn, N.; Papenmeier, J.; Applebaum, M. *J. Organomet. Chem.* **1966**, *6*, 173. (b) Abram, T. S.; Watts, W. E. *Synth. React. Inorg. Met.-Org. Chem.* **1976**, *6*, 31.

(14) All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a drybox. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Compound **1**[9b] and ferrocenylacetylene[13] were prepared as described in the literature. NMR spectra were recorded on a Bruker AM 200 instrument, and the chemical shifts are reported with reference to TMS. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer. Melting points were obtained on a HWS-SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, Göttingen, Germany. The electrochemical experiment was performed at the Institute of Inorganic Chemistry, Stuttgart, Germany. The measurements were conducted in a CH_2Cl_2 solution employing 0.1 M Bu_4NPF_6 as the supporting electrolyte. All measurements were conducted in a home-built airtight voltammetry cell with a three-electrode setup consisting of a spiral-shaped Pt auxiliary electrode and silver pseudo-reference electrode directly sealed into the side walls and a platinum working electrode, which is introduced via a central screw cap on the cell top. All other details were as described previously.[20] The formal oxidation potential, $E^{\circ\prime}$, for the reversible couple is defined as the average of the anodic and cathodic peak potentials. Preparation of **2**: To a suspension of **1** (0.42 g, 0.50 mmol) in toluene (30 mL) was added ferrocenylacetylene (0.64 g, 3.05 mmol) at room temperature. The reaction mixture was stirred for 1 h at room temperature before refluxing it until the evolution of H_2 ceased. The resultant solution was filtered and kept for crystallization at room temperature to obtain reddish brown crystals of **2** (0.54 g, yield 52%). Mp: 297 °C dec. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ 6.70–7.00 (br, 18H; C_4H_3S), 4.33 (t, ^3J(H,H) = 2 Hz, 12H; C_5H_4), 3.83 (t, ^3J(H,H) = 2 Hz, 12H; C_5H_4), 4.22 (s, 12H; CH_2), 4.08 ppm (s, 30H, Cp). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 137.88, 129.01, 128.20, 125.30 (C_4H_3S), 82.65 (Al–C≡C), 74.09, 72.00, 68.83 (C_5H_4), 70.26 (Cp), 64.81 (Al–C), 40.28 ppm (CH_2). IR (KBr, Nujol): $\tilde{\nu}$ 2119 (s), 1411 (m), 1261 (m), 1235 (w), 1223 (m), 1150 (w), 1106 (s), 1079 (w), 1001 (w), 921 (m), 875 (w), 852 (w), 819 (m), 752 (w), 536 (m), 475 (w), 452 (w) cm^{-1}. In the EI-MS spectrum only small fragments were found. Anal. Calcd for $C_{102}H_{84}Al_6Fe_6N_6S_6$ (2083.15): C, 58.81; H, 4.06; N, 4.03. Found: C, 57.86; H, 4.38; N, 4.23.

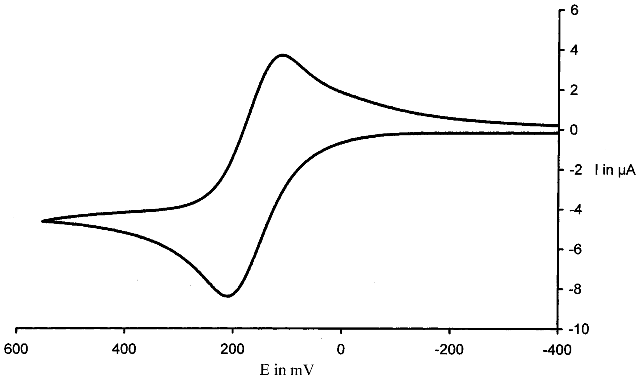


Figure 2. Cyclic voltammogram of compound **2** in CH_2Cl_2 in the presence of Cp_2Fe and decamethylferrocene as internal standards.

also deviate from linearity (C(4)−C(5)−C(6) = 174.70(7)°, C(7)−C(8)−C(9) = 176.90(8)°, C(1)−C(2)−C(3) = 174.9(8)°).

The electrochemistry of **2** was investigated in CH_2Cl_2 solution. Only one oxidation wave was observed within the solvent window (Figure 2). This was fully reversible, even at sweep rates as low as 25 mV/s, and displayed a half wave potential of +0.16 V when calibrated against the ferrocene/ferrocenium couple. The forward peak width at half-height and the peak-to-peak separation were identical with those measured for the internal ferrocene[17] and decamethylferrocene[18] standards, which were added in concentrations that can provide peak currents identical with those of compound **2**. The same overall behavior was found in differential pulse and Osteryoung square wave voltammetry. Here the peak widths at half-height fully agreed with those of both of the internal standards. From this we conclude that all six equivalent ferrocenyl subunits present in **2** are oxidized at the very same potential. The reversible electrochemical behavior of compound **2** shows that this compound is perfectly stable and robust, even in the oxidized state. These results argue against any electronic interactions between the individual ferrocenyl subunits. In diferrocenylacetylene and related systems ethynyl spacers have been found to provide a pathway for at least some degree of electronic coupling between the bridged sites.[19] Since no coupling between the ferrocenyl subunits is detected in compound **2**, the nitrogen atoms at the other end of the acetylene spacer are probably well insulated from each other by the interspersed RAl bridges.

In summary, we have synthesized and structurally studied an Al−N cluster containing six ferrocenylacetylene moieties. The electrochemical behavior of this compound shows a single reversible oxidation wave, which suggests the electrochemical equivalence of the ferrocenylacetylene moieties. This molecule can also be viewed as a system that can act as a multielectron source, electron-transfer mediator, and ion sensor. It can be taken as a model compound for the synthesis of potential molecular units containing active metal centers, which can be employed effectively in catalysis. Moreover, this paper initiates research for using metal nitrides as supports for catalysts.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften. N.D.R. thanks the Alexander von Humboldt-Stiftung for a research fellowship.

Supporting Information Available: Tables giving single-crystal X-ray structural data of compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030348D

---

(15) Szymanski, H. A. *Interpreted Infrared Spectra*; Plenum Press: New York. 1966; Vol. 2, p 5.

(16) A.suitable crystal of compound **2** was mounted on a glass fiber and coated with paraffin oil. Diffraction data for **2** were collected on a STOE IPDS II diffractometer at 133(2) K. The measurement was made with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The structure was solved by direct methods using SHELXS-97[23] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[24] All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors (including anomalous scattering) were taken from ref 25. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. Crystallographic data for $\mathbf{2}\cdot 4C_6H_5CH_3$ ($C_{130}H_{116}Al_6Fe_6N_6S_6$): $M_r = 2451.63$, triclinic, $P\bar{1}$, $a = 13.863(3)$ Å, $b = 14.790(3)$ Å, $c = 16.274(3)$ Å, $\alpha = 75.28(3)°$, $\beta = 87.05(3)°$, $\gamma = 63.63(3)°$, $V = 2884.2(10)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.411$ Mg m^{-3}, $3.28 \leq 2\theta \leq 49.72°$, $T = 133(2)$ K, $\lambda = 0.710\,73$ Å, $\mu = 0.943$ mm^{-1}, $F(000) = 1268$, 21 013 reflections collected, 8734 of which were independent and were used in the structure refinement of 716, R1 = 0.0536 ($I > 2\sigma(I)$), wR2 = 0.0867 (all data), minimum/maximum residual electron density 0.486/−0.444 e Å^{-3}. CCDC-206298 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (internat.) +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk).

(17) (a) Holloway, J. D. L.; Geiger, W. E. *J. Am. Chem. Soc.* **1980**, *101*, 2038. (b) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(18) (a) Gale, R. J.; Singh, P. *J. Organomet. Chem.* **1980**, *199*, C44. (b) Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689.

(19) LeVanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

(20) Winter, R. F.; Hornung, F. M. *Organometallics* **1999**, *18*, 4005.

(21) Park, J. E.; Bae, B.-J.; Kim, Y.; Park, J. T.; Suh, I.-H. *Organometallics* **1999**, *18*, 1059.

(22) (a) Al-Wassil, A.-A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1929 and references therein. (b) Piero, G. D.; Cucinella, S.; Cesari, M. *J. Organomet. Chem.* **1979**, *173*, 263 and references therein.

(23) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(24) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(25) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1969; Vol. IV, pp 55, 99, 149.